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STIMULATED MANDEL'SHTAM–BRILLOUIN SCATTERING AND THE PROPAGATION OF HYPERSOUND IN VISCOUS LIQUIDS

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Stimulated Mandel'shtam–Brillouin scattering was employed for studying the propagation of hypersound of frequency $\sim 8.10^9$ Hz in liquid triacetin and 1.2-propylene glycol when the viscosity of the liquids was varied by approximately seven orders of magnitude. A 50% sound-velocity dispersion was observed for triacetin and 42% dispersion for 1.2 propylene glycol. The so-called "equalization" time was found for both liquids and its temperature dependence studied. The limiting sound velocities V_∞ and V_0 were found and their temperature coefficients determined. It is found that the temperature coefficient for V_∞ is -7.6 m-sec^{-1}-deg^{-1} for triacetin and -10 m-sec^{-1}-deg^{-1} for 1.2-propylene glycol. The coefficients for V_0 are respectively -3 m-sec^{-1}-deg^{-1} and -3.2 m-sec^{-1}-deg^{-1}. The phenomenon cannot be described by the relaxation theory but can be described satisfactorily by the nonlocal theory of sound propagation in viscous media.

A STUDY of the propagation of sound in viscous media in the ultrasonic and the hypersonic regions[1-3] has led to the establishment of a dependence of the velocity of sound on the frequency and on the time of viscosity relaxation. These experimentally established regularities have shown clearly that the relaxation theory,[4] which describes well the propagation of sound in low-viscosity media, is unsuitable in principle for the description of the propagation of sound in liquids characterized by large viscosity.[1,5] The conclusions of [1] were the basis of a theory of sound propagation in viscous liquid, developed by Isakovich and Chaban,[6,7] which will be referred to later.

It is very important for the investigation of the amorphous state to extend the study of the velocity and absorption of sound to very high hypersonic frequencies and to very low infrasonic frequencies. A study of the propagation of hypersound artificially generated by piezoelectric quartz or by other emitters in viscous media is utterly impossible at present, owing to the tremendous absorption. Therefore, the only way of obtaining the desired results at present is to investigate the propagation of hypersound by studying the fine structure of the light-scattering line.[5] Some results in this direction were obtained in the study of the thermal-scattering spectrum excited by mercury lamps.[2,3,5] Now that lasers are in use, an experimental investigation of this problem can be greatly facilitated and expanded.

This investigation is the first attempt to study the dependence of the hypersound propagation velocity on the temperature (viscosity) in liquids on the basis of an investigation of the spectra of stimulated Mandel'shtam–Brillouin scattering (SMBS) in these media.1) We investigated SMBS in triacetin and 1,2-propylene glycol, at viscosities ranging from several hundredths of a poise to 10^5 poise.

INVESTIGATION METHOD AND MEASUREMENT ERROR

The stimulated Mandel'shtam–Brillouin scattering was observed in triacetin and 1,2-propylene glycol in a special cell, the construction of which is clear from Fig. 1. The liquids were first purefied by dehydration and distillation in vacuum, and then poured into the vessel of Fig. 1. By blowing a jet of cold nitrogen gas between the double walls of the vessel, the liquid could be cooled to the required temperature. The heating was by circulating water between the same double walls of the vessel, the water temperature being varied with the aid of a Heppler thermostat. Vacuum gaps on both ends of the vessel protected the input and output windows from fogging at low temperatures.

Light from a giant pulse (60 MW, 12 nsec duration, spectral width 0.03 cm^{-1}) from a ruby laser of the same type as described in [8] was focused by a lens f = 5 cm inside the vessel with the scattering medium. The SMBS light, scattered at $\theta = 180°$, was amplified in the ruby

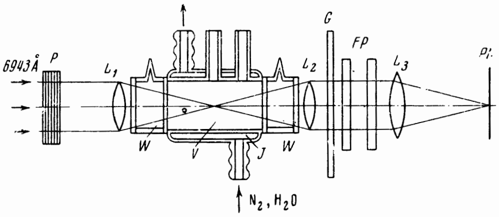

FIG. 1. Diagram of setup: P–stack of plates attenuating the ruby-laser radiation, V–scattering volume, J–jacket for thermostatic control, W–vacuum volume of cell, L_1, L_2–lenses (f = 5 cm), G–ground-glass plate, FP–Fabry-Perot interferometer, L_3–objective (f = 160 cm), P–photographic plate.

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1) The viscosity of the medium, generally speaking, can depend on the electric field intensity, which is appreciable in SMBS. However, the results of the measurements of the velocity of hypersound obtained from SMBS practically coincide with results obtained with thermal scattering, thus apparently indicating that this effect is not very significant under our conditions.

laser and directed to the Fabry-Perot interferometer (Fig. 1). Behind the interferometer was a camera, whose lens has a focal length 160 cm. The SMBS spectrum was photographed on A-700 film.

As established by Mash, Morozov, Starunov, and one of the authors of this paper,[9] the position of the component in the SMBS spectrum excited by a pulse of a single-mode laser depends essentially on the intensity of the exciting light and is practically the same whether feedback is produced between the scattering volume and the laser or not. We therefore chose in this experiment the intensity of the exciting light in such a way that the spectrum was obtained at the threshold of the SMBS observation. The light of the exciting laser pulse was attenuated by a stack containing varying number of glass plates. The largest possible error as a result of "capture" of the SMBS component[10] in our optical resonator was less than 5×10^{-3} cm^{-1}.

In all cases we chose for the reduction spectra in which there is only one Stokes SMBS component. Successive and repeated scattering[9] did not appear in these cases on the photographs of the spectrum. Photographs of the SMBS spectra in triacetin and 1,2-propylene glycol at various temperatures are shown in Fig. 2.

The velocity of the hypersound was calculated by means of the formula

$$V = c\Delta\nu\Lambda = 1.041 \cdot 10^6 \frac{\Delta\nu}{n}, \qquad (1)$$

where $\Delta\nu$ is the frequency shift of the SMBS component, determined by the off-center method,[5] c is the speed of light, and $\Lambda = \lambda/2n \sin(\theta/2)$ is the wavelength of hypersound; the numerical coefficient 1.04×10^6 in (1) is obtained for the case $\theta = 180°$ and $\lambda = 6943$ Å.

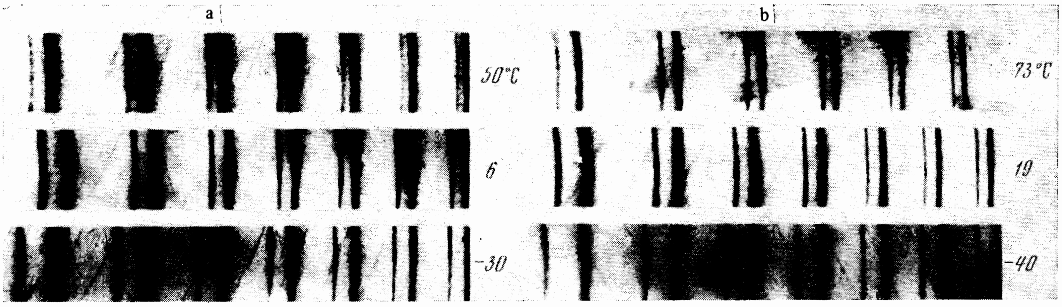

FIG. 2. SMBS spectra in triacetin (a) and in 1, 2-propylene glycol (b) at three temperatures.

The principal random error in the determination of the speed of sound is due to the error in the determination of $\Delta\nu$. An estimate shows that the error differs somewhat for different temperatures and amounts to ~2% of the measured velocity of hypersound.

MEASUREMENT RESULTS

The results of measurements of the velocity of hypersound in triacetin and in 1,2-propylene glycol are listed in Table I and are shown also in Figs. 3 and 4.[2)] The viscosities of these substances were measured earlier.[1]

Figure 3 shows for comparison, besides the experimental values of the hypersound velocity obtained from the SMBS spectra (◑), also the data obtained from the thermal scattering spectra (•),[3] as well as data for ultrasound (○).[1] In Fig. 4, the experimental data for the dependence of the velocity of hypersound on the temperature, obtained from the SMBS spectra (●), are compared with the experimental data for the temperature dependence of the velocity of the ultrasound (○).[1] The viscosities ranged from 0.02 to 10^6 poise in the case of hypersound and from 0.2 to 10^8 poise in the case of ultrasound.

In agreement with the earlier investigations, the temperature coefficients of the limiting values of the speed of sound V_∞ and V_0 (see Figs. 3 and 4) are different, with $\Delta V_0/\Delta T < \Delta V_\infty/\Delta T$. Certain differences in the values of $\Delta V_\infty/\Delta T$ for triacetin, obtained from the spectra of thermal and stimulated scattering, lie within the limits of errors of both experiments. In the ultrasonic and hypersonic regions the temperature coefficients of the velocity practically coincide.

Table I. Results of measurement of the velocity of hypersound

Triacetin		1, 2-propylene glycol	
T, °C	V, m/sec	T, °C	V, m/sec
+60	1316	+81	1294
+41.5	1373	+73	1343
+33	1401	+58	1405
+20	1570	+49	1461
+9	1678	+35	1594
+6	1824	+19	1885
+2	2000	+17.7	1850
−6	2065	+11	1990
−20	2240	+2.5	2128
−22	2294	−8	2263
−30	2350	−11.2	2361
−49	2549	−20.5	2454
		−31	2544
		−40.5	2655
		−46	2712
		−55	2800

The ultrasound velocity was investigated at 3 MHz, and the frequency was kept constant in the entire interval of temperature (viscosity) measurement. In the case of the hypersound measurements, the situation is much more complicated. It is clear from the formula given above for Λ and for the frequency

$$\Omega = V/\Lambda = 2nV/\lambda,$$

that V and n depend on the temperature, with V de-

[2)] Some of our experiments indicate that the character of the temperature dependence of the velocity of hypersound depends on the "history" of the sample. This question is now under study.

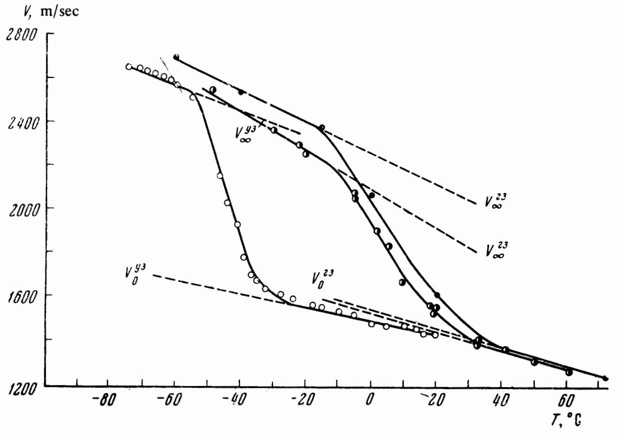

FIG. 3. Temperature dependence of the propagation velocity of ultrasound from [1] (○), hypersound from SMBS (◑), and hypersound from thermal scattering [2,3] (●) in triacetin. Solid lines–result of calculation by the formulas of the theory of Isakovich and Chaban [7].

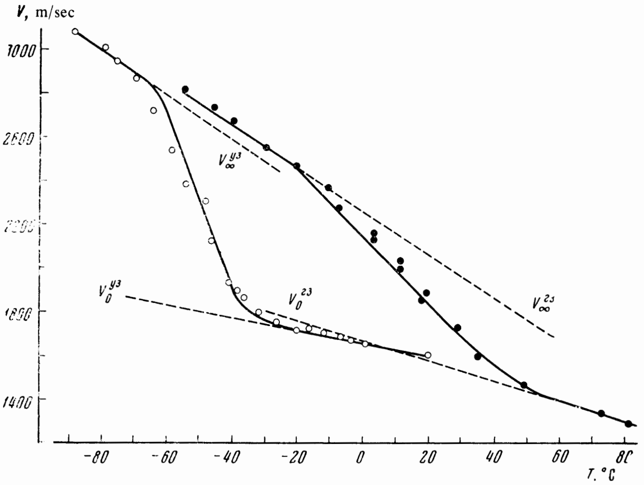

FIG. 4. Dependence of the propagation velocity of ultrasound [1] (○) and hypersound from SMBS (●) on the temperature in 1, 2-propylene glycol. Solid lines–result of calculations by the formulas of [7].

pending on the temperature quite strongly (see Figs. 3 and 4). Thus, each temperature has its own hypersound frequency. This is a shortcoming of both the thermal and stimulated scattering methods. So far, however, these remain the only methods of measuring the velocity and absorption of hypersound in liquids, particularly in viscous liquids.

The dependence of the velocity of hypersound and ultrasound on the temperature is essentially similar to the dependence on the frequency. Indeed, as already noted earlier,[1] it can be assumed that the relaxation time is $\tau_r = B\eta/t$, where B is a constant which is practically the same for all liquids, and η and T are the viscosity and the absolute temperature. In both investigated liquids, the absolute temperature changed by approximately 45%, whereas the viscosity η and consequently the frequency $\Omega = 1/\tau_r$ changed by seven orders of magnitude. We can therefore neglect, in first approximation, a change of approximately 100% in the hypersonic frequency, and we can speak of the dispersion of the speed of sound in the case of ultrasonic and hypersonic measurements.

Taking into consideration the extrapolation of V_0 to a temperature at which the strong variation of the curve gives way to a slowly increasing straight line V_∞ (Figs. 3 and 4) we obtain the values of the dispersion of the sound velocity, $d = (V_\infty - V_0)/V_0$, listed in Table II. A certain difference in dispersion between the ultrasonic and hypersonic regions is natural. The reasons for such a discrepancy will be discussed below.

DISCUSSION OF RESULTS

The plots of the ultrasound and hypersound velocities shown in Figs. 3 and 4 for triacetin and 1,2-propylene glycol, appear at first glance to be curves of the relaxation time.[1,5] However, a quantitative comparison of the experimental results with the relaxation theory, using a single relaxation time, shows that the initial impression is misleading.

We have compared the experimental data for the velocity of hypersound in triacetin and in 1,2-propylene glycol with the formulas of the relaxation theory, transforming them in a manner convenient for such a comparison:[1]

$$y = \frac{C}{1-C} = \Omega^2\tau_r^2, \quad C = \frac{V^2 - V_0^2}{V_\infty^2 - V_0^2}. \tag{2}$$

Such a transformation of the known formula of the relaxation theory is convenient also because y is a linear function of Ω^2 and τ_r^2, and consequently even small deviations from such a dependence can be readily caught, and because Ω and τ_r enter in the form of a product. Consequently the theory predicts the same law of variation of y, regardless of whether τ_r or Ω changes.

The result of the reduction of the experimental data in accordance with formula (2) are shown by crosses in Fig. 5. The solid curves are drawn through the experimental points, and the dashed curves are theoretical and correspond to formula (2). Consequently, a linear relation between y and τ_r is observed in the liquid, but with a slope different from that given by formula (2).

The experimental curve, as earlier in our investigations devoted principally to ultrasound, are described by the formula

$$y = \Omega\tau_r. \tag{3}$$

The relation given by (3) completely contradicts the re-

Table II. Dispersion of speed of sound.

Substance	Ultrasound		Hypersound			
	$\Omega\cdot10^{-6}$	d	$\Omega\cdot10^{-9}$	d	$\frac{\Delta V_\infty}{\Delta T}$	$\frac{\Delta V_0}{\Delta T}$
Triacetin	3	0.55	7.7	0.50	—7.6	—3
1, 2-propylene glycol	3	0,54	8,3	0.42	—10	—3.2

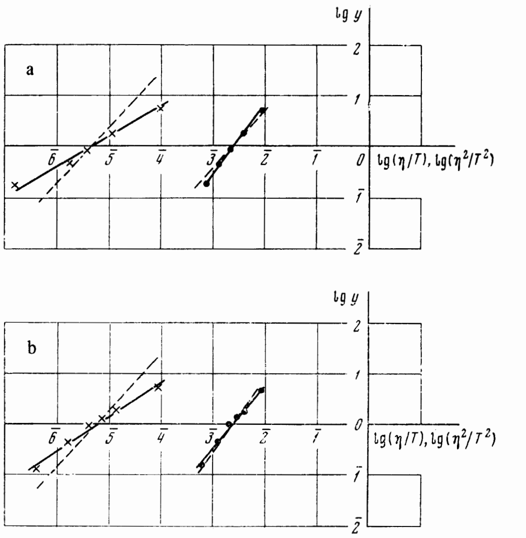

FIG. 5. Dependence of log y and log (η/T) (crosses) and log (η^2/T^2) (points): a—in triacetin, b—in 1, 2 propylene glycol. Dashed lines—theoretical curves from formulas (2) and (3).

laxation theory. The experimental data reduced by formula (3) are represented in Fig. 5 by the solid line with points; the corresponding dashed line is theoretical (formula (3)). It follows from Fig. 5 that the experimental results are well described by formula (3). However, if we continue to adhere to the relaxation theory, as is done in many cases, then it becomes necessary to introduce for the description of the experimental data an entire spectrum of relaxation times, different ones for each liquid.[11] What is particularly bad is that the chosen continuous relaxation-time function is not the only one describing the obtained experimental data for the same substance. We regard such a formal mathematical description of a physical phenomenon as unsatisfactory.

Taking into account the laws governing the propagation of sound in a viscous medium, which were obtained by us earlier,[1] Isakovich and Chaban[6,7] developed a nonlocal theory of sound propagation in such media. The nonlocal theory is based on the assumption that a viscous liquid is a microscopically inhomogeneous two-phase medium. Each of the phases of such a medium is characterized, besides the ordinary thermodynamic variables, also by two additional thermodynamic variables ξ_1 and ξ_2. It is assumed that ξ_1 is an independent variable, characterizing an inhomogeneity with dimension a,[3)] and ξ_2 is a dependent thermodynamic variable, characterizing a medium in which these inhomogeneities exist. A sound wave leads to different deviations of the parameters ξ_i from equilibrium. The equalization of these quantities occurs via diffusion, the time of which is defined as $\tau = a^2/2D$, where a is the radius of the configuration characterized by the parameter ξ_1, and D is the diffusion coefficient, which is inversely proportional to the viscosity.[4)] The delay of the equalization process relative to the pressure in the sound wave leads to the absorption and dispersion of the speed of sound.

On the basis of such a picture of the absorption in an inhomogeneous medium, a phenomenological theory was developed,[6,7] the formulas of which describe well all the heretofore performed measurements of the velocity of absorption of sound, and these formulas do not contain the variables ξ_i. To discuss the results of the present investigation, we present the necessary formulas of the simplified theory of Isakovich and Chaban (in which shear is not taken into account)[7]

$$\frac{1}{V}+i\frac{\alpha}{\Omega}=\frac{1}{V_\infty}\left[1+i\frac{V_\infty^2-V_0^2}{V_0^2}F(x^2)\right]^{1/2}, \qquad (4)$$

$$z^2F(z)=\frac{3}{2}\left(1+\frac{1}{x}\right)(x-\operatorname{th}x)\frac{1}{1+\operatorname{th}x}, \qquad (5)$$

$$\tau=\frac{5}{3}\frac{\alpha_0}{\alpha_\eta}\frac{\eta}{\rho}\frac{V_\infty^2}{V_0^2}\cdot\frac{1}{V_\infty^2-V_0^2}; \qquad (6)$$

Here $z=\sqrt{\Omega\tau}$, $x = (1-i)z$, α_0 is the amplitude coefficient of absorption up to the region of rapid variation of the velocity or absorption, a is the amplitude coefficient of absorption at any frequency and temperature, and α_η is the amplitude coefficient of absorption due only to the shear viscosity.

Using the limiting values of the velocities obtained in our experiment (Figs. 3 and 4), and also taking into account the measured and calculated values of α_0 and α_η, we can compare the experimental results with calculation by means of formulas (4)–(6). The solid curves on Figs. 3 and 4 were obtained by means of the indicated calculation, and the points represent data obtained in our experiment. The agreement between theory and experiment can be regarded as good. This pertains to both ultrasonic and hypersonic measurements.[5)]

The data for the dispersion of the velocity of sound, given in Table II, indicates that this dispersion has a tendency to decrease if the change of the temperature (viscosity) is investigated by a sonic or hypersonic wave of larger frequency. This is natural if it is recognized that the limiting velocities V_0 and V_∞ have different temperature coefficients. Figure 6 shows the limiting values of the velocities V_0 and V_∞ for different temperatures. The corresponding straight lines were extrapolated until they intersected. It is clear that the higher the frequency of the sound, the closer to the intersection point will the change of velocity from V_0 to V_∞ be effected. Consequently, for lower frequency it

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[3)] According to the estimates of Isakovich and Chaban [7], the dimensions of the inhomogeneities a at a temperature 22°C in glycerine are equal to 1.22×10^{-7} cm, corresponding to an inhomogeneity volume containing 200 molecules; with further lowering of the temperature, the volume of the inhomogeneity increases to 10^3 molecules. The hypothesis of the inhomogeneous structure of viscous liquids seems to us unusual and requires a direct experimental verification.

[4)] The quantity τ, unlike the viscosity relaxation time τ_r, will be called the equalization time (diffusion equalization).

[5)] A certain discrepancy for the ultrasonic data in 1, 2-propylene glycol is apparently due to the fact that the simplified formulas of the theory were used, without account of the finite shear modulus. Allowance for this modulus apparently improved the agreement.

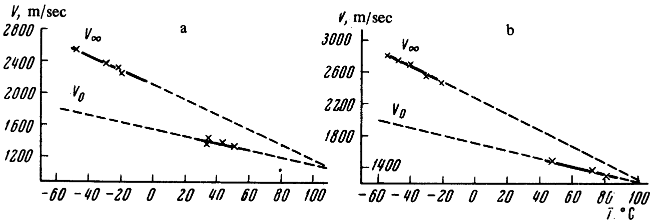

FIG. 6. Dependence of the limiting values of the velocity V_0 and V_∞ on the temperature in triacetin (a) and in 1, 2-propylene glycol (b).

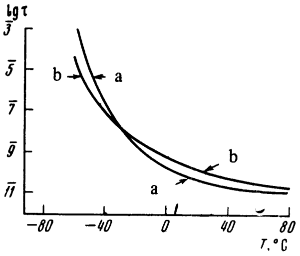

FIG. 7. Dependence of log τ on the temperature: a—for triacetin, b—for 1, 2-propylene glycol.

is necessary to expect a larger sound dispersion.

The rate of equalization of the thermodynamic quantities ξ_i is determined by formula (6), which contains the limiting values of the velocities V_0 and V_∞, measured in the low-frequency region of the sound absorption α_0, the value of α_η calculated from the shear viscosity, and the shear viscosity η. It is important that the expression for the equalization time does not contain arbitrary parameters, and the quantities are uniquely determined from different experiments. The dependence of τ on the temperature in our experiment is shown in Fig. 7.

In the experiments of Knollmann and Hamamoto,[11] dealing with the propagation of transverse intrasound (from 0.01 to 10^5 Hz) in 1,3-butanediole, 2,3-butanediole, glycerine, and in two polymers—arochlor 460 and 2442—good agreement was obtained between the experimental data and the conclusions of the theory of Isakovich and Chaban.

It must be concluded from the foregoing that the theory of Isakovich and Chaban, operating with a single non-arbitrary parameter (formula (6)), which has a definite physical meaning for pure liquids, provides a good description of the propagation of sound in viscous media in a wide frequency interval.

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